Phase Diagram of Cu–Au-Type Alloys[1]

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We investigate the ordering phase diagram of an binary alloy on a face centered cubic lattice. In Ising spin language the nearest-neighbor interactions are antiferromagnetic with strength J, the next-nearest-neighbor interactions are ferromagnetic with strength αJ, and the external magnetic field is h. For $\alpha > 0$ and all h, the ground state is only finitely degenerate, so Pirogov–Sinai theory gives the exact form of the phase diagram in the limit of vanishing temperature. For $\alpha = 0$ and $|h| \leqslant 12J$ the ground state is infinitely degenerate, and indeed the zero temperature entropy is nonvanishing at the four "super-degenerate" points $h = \pm 4J$ or $\pm 12J$. We investigate the finite temperature behavior of the model using Monte Carlo simulations and (for $\alpha = 0$) low temperature expansions. The most interesting portions of the phase diagram are those near the super-degenerate points. We rigorously map these points onto certain "hard constraint" lattice gases, but can draw no firm conclusions concerning the phase diagram in their vicinity.

1. INTRODUCTION

The study of phase transitions was one of Ilya M. Lifshitz's lifelong interests. His contributions to the subject have been both deep and extensive, and his death deprived the field of one of its most creative practitioners. This paper investigates some aspects of the phase diagram of a binary alloy on a face centered cubic (fcc) lattice, a problem to which Lifshitz made important early contributions.[1,2] It is dedicated to his memory.

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The phase diagram of an ordering binary alloy on an fcc latice has been the subject of many investigations.[1-22] Nevertheless, some of its important features remain unresolved. We report here results from Monte Carlo simulations and low-temperature expansions which shed some light upon, but which do not settle, these questions. Some exact theoretical results are also presented.

The model we consider is most easily described in Ising spin language. At each site of the lattice there is a spin variable $\sigma_i = \pm 1$, the value of which corresponds to occupation by either of the two species (A or B) of atoms. We assume an interaction Hamiltonian of the form

$$H = J \sum_{nn} \sigma_i \sigma_j - \alpha J \sum_{nnn} \sigma_i \sigma_j - h \sum \sigma_i \tag{1}$$

where the first sum ranges over nearest-neighbor (nn) and the second over next-nearest-neighbor (nnn) pairs of sites (with periodic boundary conditions). The coupling constants $J > 0$ and $\alpha J \geqslant 0$ correspond to antiferromagnetic nn interactions and to ferromagnetic (or vanishing) nnn interactions. The external magnetic field h represents, in the alloy language, the difference between the chemical potentials of the two atomic species. By symmetry it is sufficient to consider $h \geqslant 0$. (More general interactions are also of interest and are under investigation[23-25]).

The character of the ordering and transitions of this Ising model is directly related to the highly interlocked structure of the fcc lattice. In contrast with the "open" body centered cubic (bcc) and simple cubic (sc) lattices, which may be decomposed into two interpenetrating simple cubic lattices, the fcc lattice is composed of four such sublattices. A site on one sublattice has four nearest neighbors on each of the three other sublattices, for a total of 12, and six next-nearest neighbors, all on its own sublattice. The nearest-neighbor interactions, being antiferromagnetic, act to magnetize each of the four sublattices in different directions, but this is impossible because only two spin directions are available: the system is said to be *frustrated*. A more detailed analysis of the $\alpha = 0$ ground states[3,26,27] reveals that when $|h| < 4J$ the ground state consists of $(\frac{1}{2}, 0, 0)$ planes, each antiferromagnetically ordered within the plane, but with no order between the planes. Similarly, when $4J < h < 12J$ the ground state $(\frac{1}{2}, 0, 0)$ planes alternate between ferromagnetic order (with all spins up) and antiferromagnetic order, again with no correlation from one antiferromagnetically ordered plane to another. The degeneracy of such ground states is thus of order 2^L, where L is a linear dimension of the system, and the resulting entropy per spin vanishes. The ground states at the so called *super-degenerate* points $h = 4J$ and $h = 12J$ are more complex (see

Section 4): they are so degenerate that the system violates the third law of thermodynamics and has finite zero temperature entropy. Finally, for $h > 12J$ the field dominates and there is only one ground state, in which all spins point up.

The ground states are easier to describe when $\alpha > 0$. For $h < 4J$ only six of the infinitely many $\alpha = 0$ ground states remain ground states, namely, those with the metallurgist's "AB" or "$L1_0$" structure. In such states two of the four simple cubic sublattices are occupied by A atoms (i.e., up spins) and two by B atoms (i.e., down spins). The sixfold degeneracy simply reflects the $(4)(3)/2!$ ways to choose two sublattices out of four. For $4J < h < 12J$ the ground state consists of three sublattices of A atoms and one of B atoms (the "A_3B" or "$L1_2$" structure), so it is fourfold degenerate. For $h > 12J$ all spins point up. In contrast to the situation at $\alpha = 0$, the ground states at $h = 4J$ and $12J$ are now simply those of either side, so the degeneracy is tenfold at $4J$ and fivefold at $12J$.

The low-temperature states of a system usually represent a small perturbation upon its ground states. This observation is made rigorous and precise by Pirogov–Sinai theory,[27–30] which permits exact calculation of phase diagrams *at sufficiently low temperatures*, provided that two conditions are met. These conditions are, first, that there exist only a finite number of (periodic) ground states, say, $g_1, ..., g_r$, and second, that the ground states satisfy "Peierls' condition." In physical terms, Peierls' condition simply requires that the energy cost of putting a piece of one ground state inside a lattice of a different ground state be proportional to the surface area separating the two. More formally, if one begins with an infinite lattice in ground state g_i, and changes the configuration in some finite region Λ to that of ground state g_j, $j \neq i$, then Peierls' condition demands that the energy increase ΔU be greater that the surface area of Λ times some positive constant.

One may easily check that Pirogov–Sinai theory applies to the fcc Ising model when $\alpha > 0$. (In fact because of symmetry the system behaves as if it had only one ground state when $h \neq \pm 4J$, $\pm 12J$, and two ground states at those points.) The theory may thus be used to check the correctness, at low temperatures, of the approximate phase diagrams produced by Monte Carlo (MC) simulations[12–22] or by Kikuchi's cluster variation method (CVM).[5–10] Portions of the full (h, T, α) phase diagram, as obtained by MC simulation, are shown in Fig. 1 and 2. Both MC and CVM techniques predict that all the phase boundaries shown are first order, except that when α is sufficiently large (greater than about 0.3) and h vanishes exactly, the transition is continuous.

The low-temperature features of the phase diagrams in Fig. 1 and 2 are readily understood on the basis of Pirogov–Sinai theory. For example, the
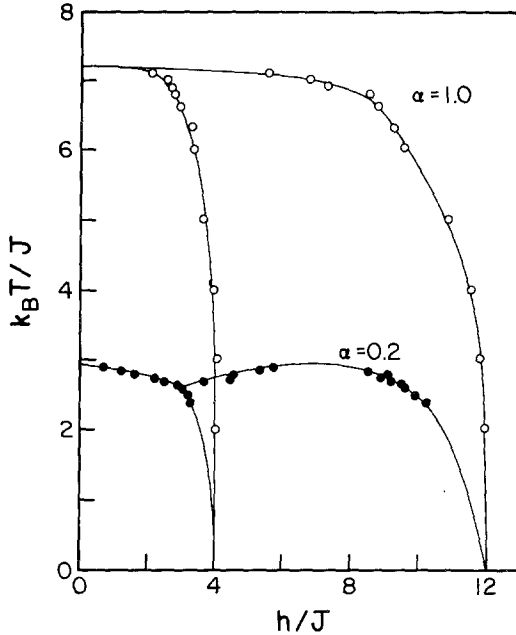
Fig. 1. Phase diagram determined by the Monte Carlo studies of Binder, Kinzel, and Selke,[16,19] showing the change in topology as α passes through α_c. All the phase boundaries shown are first order, except for the transition at $h = 0$, $\alpha = 1.0$.

coexistence line springing from $h = 4J$, $T = 0$ bends *toward* the AB phase, so that when $h = 4J$ and T is small but nonvanishing, the system is in the A_3B phase. This follows from the fact that the A_3B structure possesses more low-energy excitations than the AB structure does. Specifically, the lowest energy excitation of the A_3B structure is formed by overturning a single up spin, while the lowest energy excitation of the AB structure is formed by over-turning a single down spin. (Either of these excitations has an energy cost of $12\alpha J$ when $h = 4J$.) Thus, on a lattice of N sites, $\frac{3}{4}N$ lowest energy excitations of the A_3B structure are possible, while the corresponding number for the AB structure is $\frac{1}{2}N$. The theory also predicts that the slope of the AB–A_3B coexistence line diverges exponentially as $T \to 0$. In addition to these $\alpha > 0$ results, Slawny[31] has urged convincingly that the low-temperature equilibrium states at $h = 0$, $\alpha = 0$ will possess the same AB structure shown at $h = 0$, $\alpha > 0$. He reasoned by pointing out that, among the infinite number of possible ground states, the six AB ground states have the highest density of low-energy excitations and hence will be the only states that "survive" the transition from zero to finite temperature. This argument is easily extended to nonzero field, but it is not rigorous because Pirogov–Sinai theory has not, at present, been proven to hold in systems
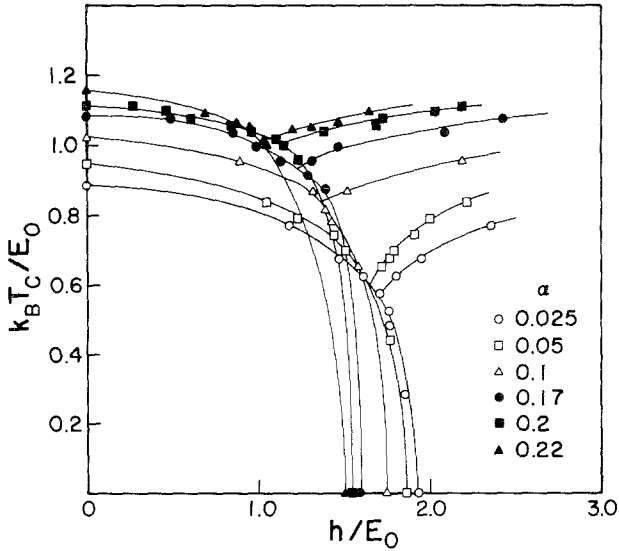
Fig. 2. Monte Carlo phase diagrams for various values of α less than α_c. To prevent crowding of the figure, the field and temperature are normalized by the zero field ground state energy $E_0 = (2 + 3\alpha)J$. The points for $\alpha = 0.2$ were taken from Ref. 19.

with infinite ground state degeneracy. There is, however, every reason to believe that Slawny's argument will produce the correct equilibrium phases at *low* temperatures and for fields *away* from the super-degenerate values $4J$ and $12J$.

The subtle and unresolved features of the phase diagram are those beyond the reach of Pirogov–Sinai theory, namely, the behavior near the super-degenerate points when $\alpha = 0$, and the (moderate temperature) crossover from a first order to a continuous transition at $h = 0$ and $\alpha = \alpha_c \cong 0.3$.

When α is small but positive all methods of analysis agree upon the existence of two triple points, (T_t, h_t) and $(T_t, -h_t)$, where the AB, A_3B, and disordered phases coexist. The cluster variation method,[5–10] and some Monte Carlo simulations[17,22] indicate that the finite temperature of this triple point persists down to $\alpha = 0$, while other simulations[14,15,21] suggest that the triple point temperature vanishes, allowing the disordered phase to penetrate down to $T = 0$ (see Fig. 3). (Recall that the zero temperature entropy is positive at $h = 4J$.)

If, on the other hand, α is allowed to increase, then h_t decreases and the two triple points eventually merge at $h = 0$ (see Fig. 1 and 5). This point of merger appears to coincide exactly with the multicritical point, already mentioned, where the $h = 0$ transition changes character from first order to
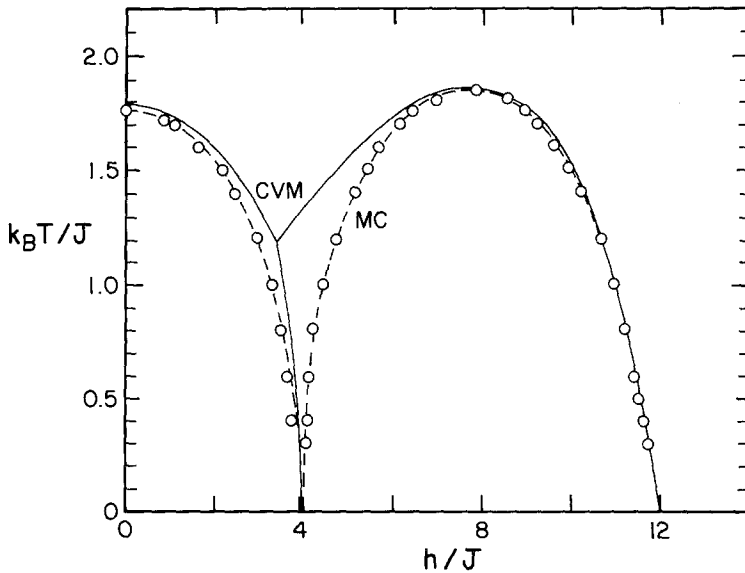
Fig. 3. Phase diagrams for $\alpha = 0$ produced by Monte Carlo (MC) simulations and by the cluster variation method (CVM). These results have been taken from Ref. 14 and 9, respectively. The super-degenerate points at $h = 4J$ and $h = 12J$ possess finite entropy at zero temperature.

continuous. The existence of this multicritical point is necessary[12,13] to allow the correct $\alpha \to \infty$ behavior, because in this limit the four interpenetrating simple cubic sublattices decouple to become four *independent* sc ferromagnetic Ising lattices, which exhibit continuous phase transitions. The idenity of the multicritical point and the merging point of the triple points was predicted by Domany, Shnidman, and Mukamel on the basis of mean field approximations and renormalization group arguments.[32] It is consistent with MC and CVM results, but is by no means an established fact.

   An outline of the remainder of this paper follows. In Section 2 we present the results of our Monte Carlo simulations and discuss their relation to previous work. We attempt to study the super-degenerate point at $h = 4J$, $\alpha = 0$, $T = 0$ by approaching it slowly from the $\alpha > 0$ side, but it is not clear whether simple extrapolation of such results to $\alpha = 0$ is justified. This section also presents a few results concerning the multicritical point near $\alpha = 0.3$. In Section 3 we use the results of Slawny[31] to derive a sixth-order low-temperature series expansion for the free energy of the $\alpha = 0$ AB phase as a function of h and T. The effective use of this expansion is, however, currently restricted to $h = 0$. In Section 4 we rigorously identify the super-degenerate

points with certain one-parameter constrained lattice gases. This maping of points onto lines may permit detailed study of the super-degenerate points. We discuss some exact results obtainable from this approach and suggest future approximate work.

2. MONTE CARLO SIMULATIONS

We performed Monte Carlo simulations on an fcc lattice of 2048 sites (a cube with eight conventional unit cells on a side), utilizing single spin flip kinetics (Glauber dynamics). Most runs were started in a disordered configuration, but some were started in the AB or A_3B structure. The simulations were generally run for 1000 Monte Carlo steps per site (MCS/site) (where a Monte Carlo step is defined as an *attempted* spin flip, whether successful or not), but in some cases 5000 or even 10 000 MCS/site were required to get out of a metastable state and reach equilibrium. The program was written in FORTRAN and used individual bits to represent spins. It was run on a CDC 7600 computer and used about 1 minute of CPU time per 10^6 attempted spin flips. Simulations were performed at $\alpha = 0.025, 0.05, 0.1, 0.17$, and 0.22. For any given α, the phase boundary was determined by measuring various thermodynamic quantities (energy, specific heat, sublattice magnetizations, and staggered susceptibilities) for a range of values of $k_B T/J$ and h/J, and looking for approximate discontinuties. In addition, the detailed structure of the configuration was used as an important indicator of the phase of the system.

Figure 2 presents our observed phase boundaries, together with those obtained by Binder[19] at $\alpha = 0.2$. As α increases the triple-point temperature $T_t(\alpha)$ slowly approaches the zero field transition temperature $T_c(\alpha)$ (see Fig. 4). A linear extrapolation of $T_t(\alpha)$ would have the two curves crossing at $\alpha_c \cong 0.35$, which is within the uncertainty range of the zero field simulation results.[12,13] Note, however, that a linear extrapolation would also require that the two curves cross, rather than merge, in complete disagreement with the expected behavior! In fact there is no reason to prefer any particular extrapolation over any other, so this value of α_c must be taken as a very rough estimate. Our results are consistent with the Domany, Shnidman, and Mukamel[32] prediction of coincidence between the merging of the triple points and the change from first-order to second-order behavior at zero field. More study is, however, required both to pin down the location of α_c and to find the critical crossover exponents there. (See also Fig. 5.)

It is even more difficult to study the $\alpha \to 0$ behavior of $T_t(\alpha)$. While a simple linear extrapolation of $T_t(\alpha)$ in Fig. 3 would yield $k_B T_t(0) \cong 0.9J$, in disagreement with previous results,[14,21] there are strong reasons to believe that this is an artifact caused by the small size of our system. For example,
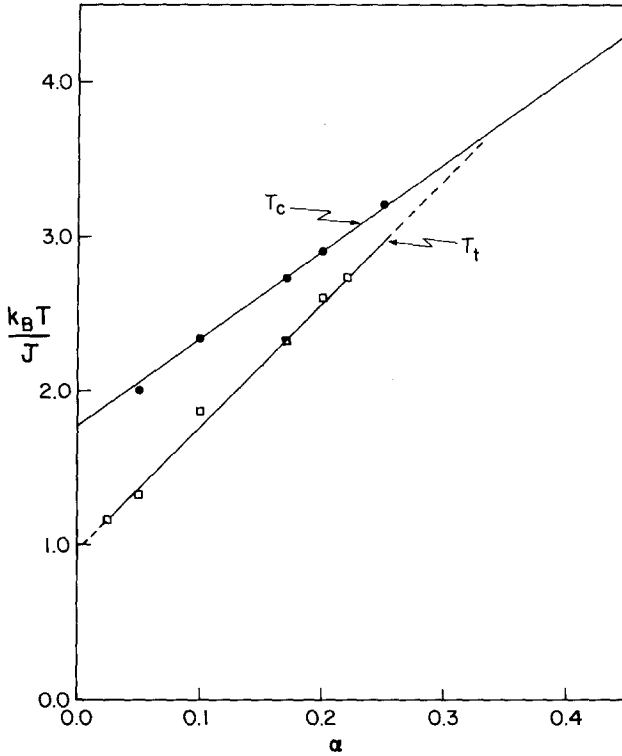
Fig. 4. The triple point temperature T_t and the zero field transition temperature T_c as functions of α.

when we performed simulations at $\alpha = 0$, $h = 4J$ for $k_B T$ between $0.4J$ and $0.6J$, we found that an $8 \times 8 \times 8$ system started in a random configuration would always order into an A_3B structure, but that a $20 \times 20 \times 20$ system would remain disordered for as long as we could wait, namely, 200 MCS/site (more than six million steps in all). Thus our results are entirely consistent with those of Binder[14] and Meirovitch.[21] Because it takes longer and longer to get out of an ordered state as the temperature decreases, one could not expect to see the disordering of an initial A_3B configuration at low temperatures even if the true phase diagram did have a disordered phase coming down to the zero temperature super-degenerate point. The question in fact cannot be resolved in any reasonably conclusive way by the kind of simulations described here. What is needed is either a different approach, such as a theory for the low-temperature phase diagram in the vicinity of a point with positive $T = 0$ entropy, or simulations done directly on the ground states. We discuss such ideas in the remaining sections.

Before leaving the simulations, however, we wish to comment upon one additional point. Note from Fig. 4 that T_c varies smoothly with α, despite the dramatic change in the character of the transition at α_c. We have discovered a remarkably accurate empirical formula for this variation. To set the stage for this formula, we first define E_0 to be the ground state energy per site, that is,

$$E_0 = (2 + 3\alpha) J \tag{2}$$

Then we form the ratio of the ground state energy due to next-nearest-neighbor bonds to the total ground state energy, and call it x:

$$x \equiv 3\alpha/(2 + 3\alpha) \tag{3}$$

This variable runs monotonically from 0 to 1 as α runs from 0 to ∞. Our formula for $T_c(x)$ is then

$$k_\mathrm{B} T_c(x)/E_0(x) = a - b(1 - x)^2 \tag{4}$$

The value of $a = 1.5036$ is fixed by the accurately known[33] transition temperature of the simple cubic ferromagnetic nearest-neighbor Ising model, to which our model reduces when $x = 1$. Setting the single adjustable parameter b to 0.62 then results in a curve which passes within 3% of all of the Monte Carlo data points. [A graph of $T_c(x)$ is presented in Fig. 7 of Ref. 13.]

3. LOW TEMPERATURE EXPANSIONS

The interesting and controversial features of the fcc Ising antiferromagnet phase diagram fall in the low-temperature regime, where Monte Carlo simulation is frequently costly and sometimes unreliable. It seems plausible that low-temperature expansions could provide better approximate data or, perhaps, even exact results in this limit. We have generated low-temperature expansions for the $|h| < 4J$ ground state in the case $\alpha = 0$, but they are less useful than one might at first suppose.

As mentioned in the Introduction, the ground state is infinitely degenerate when $\alpha = 0$ and $|h| < 4J$. Which of these many configurations should be used as a starting point for the expansion? An empirical approach would be to first expand about each ground state, and then average these expansions, giving equal weight to every possible ground state.[34,35] Although this approach seems reasonable, Slawny[31] has proven that (in those cases to which Pirogov–Sinai theory apply) it is wrong. The correct low-temperature expansion is instead produced by expanding about that
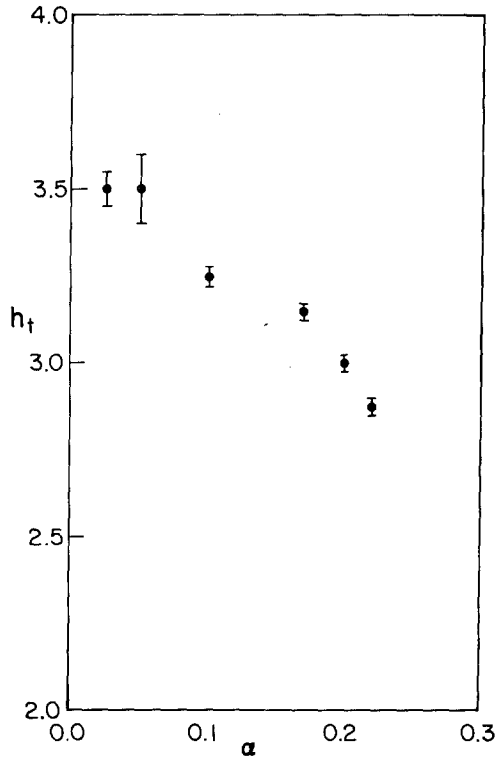
Fig. 5.   Variation of the triple point field with α.

ground state which supports the largest number of low-energy excitations. (This conclusion can be understood on physical grounds: At zero temperature no ground state is preferred because entropy makes no contribution to the free energy and all the ground states have the same energy. But at any finite temperature entropy is a factor in the free energy, and indeed it is the primary factor which differentiates the low-temperature equilibrium phases obtained as perturbations of the ground states. Hence the ground state which can contribute most to the entropy, i.e., the one with the greatest number of possible low energy excitations, will be preferred as a basis for the equilibrium states.) Although Slawny's rigorous arguments rely upon a finite degeneracy of ground states, his conclusions probably apply to our situation when $\alpha = 0$ and $|h| < 4J$, and we accept them in the following.

        In our case it transpires[4] that all of the many ground states admit the same number of lowest-energy excitations (which consist of flipping a single spin), and indeed they all admit the same number of next lowest energy excitations as well! One must examine the third level of excitations before

one finds a ground state which admits more excitations than the others. Doing this, we find that for all $|h| < 4J$ the preferred ground state is nothing other than the familiar AB structure, with two sublattices of up spins and two of down spins. We will refer to the two sublattices which, in the ground state, are occupied by up spins as the A sublattices, and to the other two as the B sublattices. One gains considerable information by assuming that the field on the A sublattices, say, h_A, is not necessarily the same as the field on the B sublattices, h_B. This permits derivation of sublattice magnetizations and staggered susceptibilities from the free energy.

In terms of the variables

$$x = e^{-4J/k_B T} \tag{5}$$

and

$$y_A = e^{-2h_A/k_B T}, \qquad y_B = e^{-2h_B/k_B T} \tag{6}$$

the free energy per site is

$$f(T, h_A, h_B) = -2J - \tfrac{1}{2}h_A + \tfrac{1}{2}h_B - k_B T g(x, y_A, y_B) \tag{7}$$

where

$$
\begin{aligned}
g(x, y_A, y_B) =\; & x^2 \left[\tfrac{1}{2}(y_A^1 + y_B^{-1}) \right] + x^3 \left[4 y_A^1 y_B^{-1} \right] \\
& + x^4 \left[-\tfrac{5}{4}(y_A^2 + y_B^{-2}) + 10(y_A^2 y_B^{-1} + y_A^1 y_B^{-2}) \right. \\
& \quad \left. + 2 y_A^2 y_B^{-2} - 4 y_A^1 y_B^{-1} \right] \\
& + x^5 \left[8(y_A^3 y_B^{-1} + y_A^1 y_B^{-3}) + (y_A^2 + y_B^{-2}) + 12(y_A^3 y_B^{-2} + y_A^2 y_B^{-3}) \right. \\
& \quad \left. - 36(y_A^2 y_B^{-1} + y_A^1 y_B^{-2}) + 4 y_A^3 y_B^{-3} + 100 y_A^2 y_B^{-2} \right] \\
& + x^6 \left[2(y_A^4 y_B^{-1} + y_A^1 y_B^{-4}) + 5\tfrac{1}{6}(y_A^3 + y_B^{-3}) \right. \\
& \quad + 26(y_A^4 y_B^{-2} + y_A^2 y_B^{-4}) - 104(y_A^3 y_B^{-1} + y_A^1 y_B^{-3}) \\
& \quad + (y_A^5 y_B^{-4} + y_A^4 y_B^{-5}) + 31(y_A^4 y_B^{-3} + y_A^3 y_B^{-4}) \\
& \quad + 342(y_A^3 y_B^{-2} + y_A^2 y_B^{-3}) + 38(y_A^2 y_B^{-1} + y_A^1 y_B^{-2}) \\
& \quad \left. + 12 y_A^4 y_B^{-4} + 204 y_A^3 y_B^{-3} - 476 y_A^2 y_B^{-2} \right] + O(x^7) \tag{8}
\end{aligned}
$$

This expansion was derived simply by overturning spins from the ground state AB configuration. Disconnected clusters of overturned spins were counted by hand, but connected clusters were enumerated by computer using a variant of the backtrack algorithm.[36] The expansion (8) should reduce to the zero-field series of Mackenzie and Young[37]: it does not because of a

minor error it that result. We are grateful to Dr. Mackenzie for examining his derivation and confirming our result. (We also mention here the zero field series of Liu *et al.*[38])

The expansion presented above clearly contains considerable configurational information on the fcc alloy problem, but it does not contain the information needed to investigate the $h = 4J$ super-degenerate point. This is readily seen by setting $T = 0$. The true $T = 0$ free energy per site is

$$f(T = 0, h_A = h_B = h) = \begin{cases} -2J, & 0 \leqslant h \leqslant 4J \\ -\tfrac{1}{2}h, & 4J \leqslant h \leqslant 12J \\ -h, & 12J \leqslant h \end{cases} \tag{9}$$

but the series cannot, of course, locate the singularities at $h = 4J$ and $12J$. It is not directly useful for investigating the super-degenerate points.

The expansion can, however, be used to obtain considerable information concerning the low-field behavior of our model. In particular, it may be compared with existing zero field, high-temperature free energy expansions to
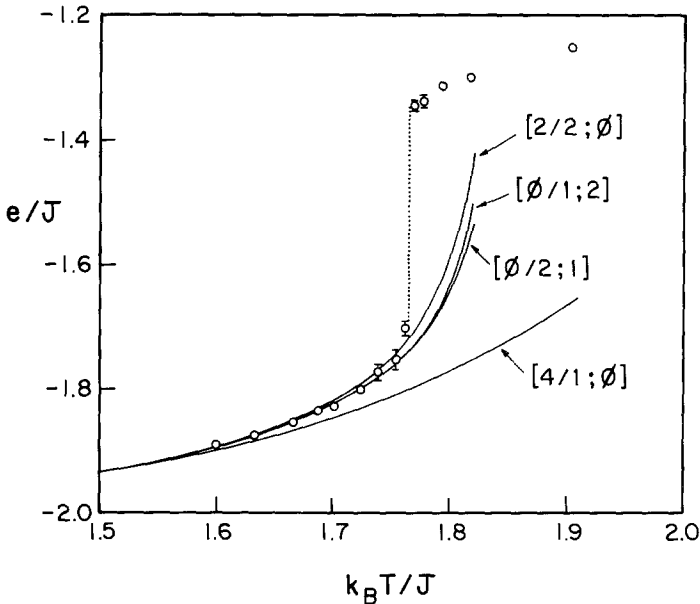

Fig. 6.   Various extrapolations of the low-temperature series for the zero field, $\alpha = 0$ energy per site, compared with the Monte Carlo data and transition temperature of Phani *et al.*[12,13] The various approximants are named according to the system established in Ref. 40: $[4/1; \varnothing]$ is a truncation of the series, $[2/2; \varnothing]$ is a direct Padé approximant, and $[\varnothing/2; 1]$ and $[\varnothing/1; 2]$ are Dlog Padé approximants.

locate and characterize the first-order phase transition. Work in this direction is currently in progress: an example of the results obtainable is presented in Fig. 6, which compares three methods[39,40] for extrapolating the low-temperature energy series with Monte Carlo results. As expected, simple truncation of the series produces a poor approximant, which underestimates the energy. A direct Padé approximant (which can accurately approximate a rational function displaying only simple poles) is closer to the Monte Carlo results, but is too high. The two Dlog Padé approximants (which can accurately approximate algebraic functions with branch point singularities) agree quite well with both the Monte Carlo points and with each other.

4. CONSTRAINED MODELS AND EXACT ARGUMENTS

We have seen that both Monte Carlo simulations and low-temperature expansions are useful tools for the fcc alloy problem but that neither tool can unambiguously describe the system near its super-degenerate points. In this section we consider a change of variable which focuses specifically on the states obtained in the limit that h and T approach a super-degenerate point along certain trajectories. This approach yields certain exact results, and it may render either of the above methods more reliable.

We rewrite Hamiltonian (1) as

$$
\begin{aligned}
H &= J \sum \sigma_i \sigma_j - \alpha J \sum \sigma_i \sigma_j - h_0 \sum \sigma_i - \delta h \sum \sigma_i \\
&\equiv H_0 - \delta h \sum \sigma_i
\end{aligned}
\tag{10}
$$

where h_0 is an arbitrarily specified field strength, and

$$
\delta h \equiv h - h_0
\tag{11}
$$

We also define

$$
z \equiv e^{-2\delta h/k_{\rm B}T}
\tag{12}
$$

so the partition function is

$$
Z = \sum_{\text{states}} e^{-H_0/k_{\rm B}T} z^{-\Sigma \sigma_i/2}
\tag{13}
$$

Contours of constant z in the $(k_{\rm B}T/J, h/J)$ plane are lines radiating from the point $(0, h_0/J)$. If such a line has slope γ, it has

$$
z = e^{-2/\gamma}
\tag{14}
$$

We now consider the limit of zero temperature with J, α, and h_0 held fixed, but with δh vanishing linearly with temperature. In other words, we approach a ground state at fixed J, α, and $h = h_0$ along one of the rays of constant z. It can be shown rigorously[41] that in this limit the equilibrium states of our antiferromagnetic system are isomorphic to the equilibrium states of a certain constrained lattice gas. To see this physically we note that in this limit the partition function (for a finite system) is

$$Z(h_0, z) = \sum z^{-\sum \sigma_i/2} \tag{15}$$

where the sum now extends *only over the ground states of H_0* (and where we have adjusted the energy zero so that $H_0 = 0$ for a ground state). This partition function defines a new statistical mechanical problem which is analyzed most conveniently in lattice gas language. To associate down spins with occupied sites we use the occupation variable

$$\rho_i = (1 - \sigma_i)/2 \tag{16}$$

so the partition function becomes

$$Z(h_0, z) = z^{-N/2} \sum z^n \tag{17}$$

where n is the number of occupied sites in a configuration. (Note that this exercise works equally well for any uniform field Ising model, regardless of the lattice or of the range and type of interaction.)

To discover the character of these lattice gas problems we must investigate the ground states of H_0. For $\alpha = 0$ this is most conveniently done[3,26,27] by dissecting the fcc lattice into its constituant tetrahedra. Each lattice site is shared by eight tetrahedra and each nearest-neighbor bond by two tetrahedra. Thus a tetrahedron with sites i, j, k, and l contributes an amount

$$\begin{aligned} E_T(\sigma_i, \sigma_j, \sigma_k, \sigma_l) \equiv \tfrac{1}{2}J(\sigma_i\sigma_j + \sigma_i\sigma_k + \sigma_i\sigma_l + \sigma_j\sigma_k + \sigma_j\sigma_l + \sigma_k\sigma_l) \\ + \tfrac{1}{8}h_0(\sigma_i + \sigma_j + \sigma_k + \sigma_l) \end{aligned} \tag{18}$$

to the Hamiltonian H_0. We then find that configuration of a single tetrahedron which minimizes E_T, and attempt to piece together such configurations to fill the entire lattice. If we can so fill the lattice, then we have found a ground state. If we cannot, then we must begin the procedure anew by dissecting the lattice into different subunits. (It transpires that only tetrahedra are needed when $\alpha = 0$, but other subunits are required when $\alpha \neq 0$.[27])

It is easy to show that the E_T minimizing configuration is a tetrahedron

with two spins up and two spins down when $|h| < 4J$, with three spins up and one down when $4h < h < 12J$, and with all spins up when $12J < h$. Geometrical packing arguments then demonstrate that the ground states are the layered configurations described in the Introduction. The corresponding "ground state problems" defined by (17) are thus one dimensional in character. The situation is different at the super-degenerate points. When $h = 12J$, the permitted tetrahedra have either one or zero down spins. A down spin corresponds to an occupied site, so in lattice gas language this restriction simply means that the nearest neighbors of an occupied site cannot be occupied. The ground state problem at $h = 12J$ is simply the hard "sphere" problem on an fcc lattice! The phase transition of the hard sphere model is simply the $T \to 0$ limit of the first-order phase boundary shown in Fig. 3, and the critical activity of the hard sphere lattice gas gives the limiting slope of the $k_B T/J$ vs. h/J coexistence line by Eq. (14). More information on the phase coexistence line, such as its limiting curvature, could be obtained by investigating the "soft sphere" lattice gas problem in which the nearest-neighbor repulsive interaction is strong but not infinite.

On the other hand when $h = 4J$ the permitted tetrahedra have either one or two down spins, so an occupied site may have from zero to four nearest neighbors. (This problem is not, however, equivalent to a lattice gas in which each atom has a maximum of four nearest neighbors.) The number of down spins (occupied sites) on an N site lattice can range from $\frac{1}{4}N$ to $\frac{1}{2}N$. We refer to models of this type as "hard constraint" lattice gases, the constraint being the occupation number restriction for each tetrahedron. As before, information about the hard constraint model can be transcribed to the antiferromagnet problem at $T = 0$, and more information can be gained by relaxing slightly the constraint.

What may we expect to find upon analysis of the hard constraint lattice gas corresponding to the $h = 4J$ super-degenerate point? Three possibilities seem reasonable: First, if the $\alpha = 0$ phase diagram displays a finite-temperature triple point (as in the solid curve of Fig. 3) then the lattice gas will show a single, presumably first-order, transition. Second, if the disordered phase penetrates to zero temperature (as in the dashed curve of Fig. 3), and the AB-disorder and disorder-A_3B phase coexistence lines spring vertically from the super-degenerate point, then the lattice gas will show a single transition at $z = 1$. Third, if the disordered phase penetrates to zero temperature but the two coexistence lines bounding it open with finite angle, then the lattice gas will show *two* transitions: with increasing activity the system will pass from A_3B order to disorder and then from disorder to AB order. This list does not, of course, exclude other possibilities, such as the coexistence of a large number of phases at the super-degenerate point (as is known to happen at the multiphase point of the ANNNI model).

The precise mapping between the thermodynamic quantities of the super-degenerate point and those of the hard constraint lattice gas follows in the usual way from (17). In particular, the grand canonical function of the lattice gas is

$$\Xi_N(z) = \sum{}' z^n \tag{19}$$

and its reduced pressure is

$$p(z) = \lim_{N \to \infty} \left[N^{-1} \log(\Xi_N(z)) \right] \tag{20}$$

The basic thermodynamic relation is

$$p(z) = s(z) + \rho(z) \log(z) \tag{21}$$

where $s(z)$ is the entropy per lattice site in units of k_B, and $\rho(z)$ is the density, obtainable from

$$\rho(z) = z(dp/dz) \tag{22}$$

The significant feature of the mapping is that the lattice gas $s(z)$, obtained through (21), is *identical* to the limit of the antiferromagnet model entropy as $J/k_B T \to 0$ along a ray with slope given by (14). We also note, for future use, that

$$\frac{d\rho}{dz} = \frac{dp}{dz} + z \frac{d^2 p}{dz^2} = \frac{\langle (n - \langle n \rangle)^2 \rangle}{zN} \tag{23}$$

is nonnegative for physical values of z (as is also clear on physical grounds).

We now prove that the maximum entropy for any hard constraint lattice gas falls at activity $z = 1$, and that the entropy is monotonic nondecreasing as z varies from 0 to 1 and monotonic nonincreasing as z varies from 1 to ∞. This implies that the limiting entropies obtained by approaching the super-degenerate point along different rays need not be identical, and that the maximum such entropy is obtained by approaching vertically. The proof is based on a variational principle over probability distributions. The standard grand canonical probability distribution $\omega_z^{eq}(\xi)$ over states ξ is given as usual by

$$\omega_z^{eq}(\xi) = z^n / \Xi(z) \tag{24}$$

In this distribution, we can calculate

$$\rho[\omega_z^{eq}] \equiv \sum_{\xi}{}' n(\xi) \, \omega_z^{eq}(\xi) \tag{25}$$

and

$$s[\omega_z^{eq}] \equiv -\sum_{\xi} \omega_z^{eq}(\xi) \log(\omega_z^{eq}(\xi)) \tag{26}$$

and they will be the same as the corresponding "thermodynamic" values of $\rho(z)$ and $s(z)$ obtained through (21) and (22). However, Eq. (25) and (26) can be evaluated in any normalized probability distribution $\omega(\xi)$. The variational principle[42] states that the pressure

$$p[z, \omega] \equiv s[\omega] + \rho[\omega] \log(z) \tag{27}$$

obtained using the equilibrium distribution ω_z^{eq} is the maximum $p[z, \omega]$ obtainable from any distribution. In particular, $p[z, \omega_z^{eq}]$ is greater than or equal to the pressure calculated using the distribution appropriate to some other value of z, say, z', so

$$s[\omega_z^{eq}] + \rho[\omega_z^{eq}] \log(z) \geqslant s[\omega_{z'}^{eq}] + \rho[\omega_{z'}^{eq}] \log(z) \tag{28}$$

or

$$s(z) - s(z') \geqslant -[\rho(z) - \rho(z')] \log(z) \tag{29}$$

We first examine the case $z' < z < 1$. From (23), the right-hand side of (29) is nonnegative, so

$$z' < z < 1 \Rightarrow s(z') \leqslant s(z) \tag{30}$$

Now take the case $z' > z > 1$. The right-hand side of (29) is again nonnegative, whence

$$z' > z > 1 \Rightarrow s(z') \leqslant s(z) \tag{31}$$

and the result is proved.

The above analysis suggests strongly that the phase coexistence line originating at $T = 0$, $h = 12$ bends toward the A_3B phase (as it does when $\alpha > 0$). Otherwise the corresponding hard constraint lattice gas would show a transition at $z < 1$, and so, by (30), the entropy would *increase* in passing from the disordered to the A_3B ordered phase! Similar arguments can be applied to the antiferromagnetic Ising model on the square and simple cubic lattices, which have super-degenerate points at $h = 4J$ and $6J$, respectively. In these cases our argument is less persuasive because the transition is expected to be continuous rather than first order. Even so, the result $z_c > 1$ is well supported by the approximate critical activities obtained from series analysis: these are $z_c = 3.7962$ and $z_c = 1.09 \pm 0.07$, respectively (as found

by Baxter, Enting, and Tsang[43] and by Gaunt[44]). Our result also argues against the reentrant transitions predicted[45] by CVM in the simple cubic antiferromagnet. On the other hand, the body centered cubic lattice has a super-degenerate point at $h = 8J$, but Gaunt[44] estimates that the corresponding lattice gas has a critical transition at $z_c = 0.77 \pm 0.05$.

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